PATENT SPECIFICATION

NO DRAWINGS

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883,024

Date of filing Complete Specification (under Section 3 (3) of the Patents Act 1949): May 21, 1958.

Application Date: May 21, 1957. *No. 16125/57.*

Application Date: Sept. 2, 1957. *No. 27633/57.*

Complete Specification Published: Nov. 22, 1961.

Index at acceptance:—Classes 82(1), A8(A1: A2: A3: J: K: M: Q: R: U: W: Y: Z2: Z5: Z8: Z12), A15A; and 72, A11D.

International Classification:—C22c. C21d.

COMPLETE SPECIFICATION

Improvements relating to Alloy Steel

We, THE UNITED STEEL COMPANIES LIMITED, a British Company, of The Mount, Broomhill, Sheffield 10, formerly of 17, Westbourne Road, Sheffield 10, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is known that by suitable control of the chemical composition of stainless steels it is possible to ensure that the austenite either does or does not transform to martensite on cooling to room temperature, the steel being austenitic if the transformation range is below room temperature and martensitic if it is above.

The production of a stainless steel in which the transformation will take place within a given narrow range is somewhat difficult because a variation in any alloying elements alters the transformation range. Moreover, nearly all alloying elements tend to form delta ferrite, which is undesirable since it leads to a reduction in strength and also makes the steel difficult to hot-work. The only alloying elements which do not tend to produce delta ferrite are carbon, nitrogen, nickel, copper, manganese and cobalt.

In the practical manufacture of complex steels the difficulty of producing a steel to a precise composition increases rapidly as the number of alloying elements to be controlled increases. If there is substantial tolerance with regard to the content of each such element, the difficulty is not great, but in stainless steels of the kind in question the tolerances permitted to the steelmaker must be small if steels of substantially identical properties are to be produced in successive heats.

Our object is to provide stainless steels which can be reproduced with consistent properties without great difficulty, and which therefore contain a minimum number of alloying elements, which contain less than 15% delta ferrite in their microstructure after suitable heat-treatment and in which the martensite transformation range lies between 30 and −90°C.

According to this invention steels contain from 0.07 to 0.16% carbon, from 14 to 17.5% chromium, from 3.5 to 4.5% nickel and not more than 0.05% nitrogen. They also contain manganese either alone or with one or more of the elements silicon, tungsten and molybdenum. It is these last-mentioned elements which are important in producing the desired properties, and the steels may be regarded as including an alloy addition X which must satisfy the following equation:—

$$X = Mn + \frac{11}{7}Si + W + \frac{2}{3}Mo = 2.5 \text{ to } 3.5,$$

where Mn etc. are the percentages of these elements.

The alloy addition X preferably consists of manganese with not more than one of the other alloying elements. The steel will obviously be cheapest if the alloy addition is either manganese alone or manganese and silicon. However, the addition of at least a proportion of the more expensive alloying elements tungsten and molybdenum may be justified because of the increased high-temperature strength which these elements give.

Within the ranges of chromium and carbon set forth above neither the highest chromium and highest carbon contents nor the lowest chromium and lowest carbon contents may be used together. It is therefore necessary to satisfy a further condition, namely that $Cr + 100C = 23.5$ to 30, where Cr and C are the percentages of these elements.

Thus in the specification of one steel (A) according to the invention the carbon content is from 0.07 to 0.11% and the chromium content from 16.5 to 17.5%. In another steel

(B), of higher tensile strength, the specification requires a carbon content of 0.11 to 0.16% and a chromium content of 14.0 to 16.5%.

In either of these steels A and B it is most convenient to make the addition X as one of the following:—

	X 1	X 2	X 3
Silicon	1.75 to 2.25	—	— %
Tungsten	—	2.5 to 3.0	— %
Manganese	up to 0.5	up to 0.5	2.5 to 3.0%

The steels according to the invention are first put into the austenitic state by a solution heat-treatment, and are fabricated in this state, being converted to the martensitic state before being put into service. The solution treatment should be effected at a temperature between 900°C. and 1,100°C. In general, in order to obtain satisfactory solution and to prevent forming too much delta ferrite a solution temperature of 1,050°C. is preferred.

The steels according to the invention must not contain more than 15% delta ferrite after cooling in air from 1,050°C. An important advantage obtained by means of the invention is that the steels have the desired transformation properties and contain no more than this amount of delta ferrite without requiring the presence (and accurate control) of more than a small number of alloying elements. However, it is well known that additions of small amounts of elements other than those mentioned above are often made in the manufacture of stainless steel, and these may be made in the manufacture of steel according to the invention, provided that the effect is neither to increase the amount of delta ferrite above 15% nor to reduce the martensite transformation range below −90°C. Particular examples are small amounts (say up to 0.2%) of each of the elements vanadium, niobium, aluminium, titanium and cobalt, but as the first four of these strongly tend to form ferrite they are preferably absent.

In the preferred steels the only elements present are carbon, chromium, nickel, nitrogen, manganese with or without either silicon or tungsten, and, of course, iron which (except for impurities) forms the balance of the composition.

Despite what has just been said the steels according to the invention may also contain copper. The reason for adding copper is that it produces a precipitation-hardening effect after the transformation to martensite. It is possible to obtain this precipitation with a heat-treatment at a temperature (450°C.) which is not high enough to produce softening of the martensite, and consequently the hardening effect obtained is additional to that produced by the martensite.

The addition of copper is, of course, disadvantageous in that the content of it must also be closely controlled. If it is present at all, except as an impurity, the amount should be at least 1%, because below this the amount of copper-rich phase which precipitates is small and consequently, the hardening effect is small. The copper content may be as high as 4%, but above this the system is so unstable that the copper-rich phase will precipitate before the martensite transformation takes place and the precipitation-hardening effect is lost. The preferred copper content is from 1.5 to 3.5%.

The presence of copper affects the equation for X, so if copper is present this equation must be modified to become:—

$$X = Mn + \frac{11}{7}Si + W + \frac{2}{3}Mo + \frac{1}{2}Cu = 2.5 \text{ to } 3.5.$$

The conversion to the martensitic state is effected by heat-treatment. One heat-treatment comprises heating to cause precipitation of chromium carbide, say to 700°C. for 2 hours. Since this lowers the amount of both chromium and carbon in solid solution, the martensite transformation range is raised. Cooling to room temperature now causes the steel to pass through the martensite range and hardening will occur. Another heat-treatment comprises cooling the steel below the transformation range, say to about −80°C.

Typical figures for the martensite range for steels A and B with alloy additions X1, X2 and X3, together with the mechanical properties which are obtainable after the two different heat-treatments, are as follows:—

	A with X1	A with X2	A with X3	B with X1
Martensite Range °C.	30 to −80	20 to −90	20 to −90	20 to −90
Tensile strength (tons/sq. inch) After				
700° C. for 2 hours	70	73	71	80
−78° C. for 1 hour	85	88	85	90

Either heat-treatment puts the steel into the essentially martensitic condition, and it is then possible to obtain some improvement in mechanical properties by a low-temperature tempering treatment between 450 and 550°C. Typical examples of the mechanical properties after this heat-treatment are given below:

	A with X1	A with X2	A with X3	B with X1
Tensile strength (Tons/sq. inch) 700° C. for 2 hours + 450° C. for 2 hours	85	82	80	95

When the alloy addition X to steels A and B is 2% manganese +2% copper, typical tensile strengths in tons per square inch obtained after the heat-treatments set forth are:—

	Steel A	Steel B
After 2 hours at 700° C. followed by 4 hours at 450° C.	80	90
After 1 hour at −78° C. followed by 4 hours at 450° C.	90	100

WHAT WE CLAIM IS:—

1. Stainless steel containing from 0.07 to 0.16% carbon, from 14 to 17.5% chromium, from 3.5 to 4.5% nickel and not more than 0.05% nitrogen, characterised by a content of manganese with or without one or more of the elements silicon, tungsten and molybdenum in an amount such that

$$Mn+\frac{11}{7}Si+W+\frac{2}{3}Mo=2.5 \text{ to } 3.5,$$

the chromium and carbon contents being such that $Cr+100C=23.5$ to 30, and the steel being also characterised by less than 15% delta ferrite in its microstructure when air-cooled after heat-treatment at 1,050°C. and having its martensite transformation range between 30 and −90°C.

2. Stainless steel containing from 0.07 to 0.16% carbon, from 14 to 17.5% chromium, from 3.5 to 4.5% nickel, not more than 0.05% nitrogen and manganese with or without one or more of the elements silicon, tungsten and molybdenum such that

$$Mn + \frac{11}{7}Si + W + \frac{2}{3}Mo = 2.5 \text{ to } 3.5,$$

with or without one or more of the elements: vanadium, niobium, aluminium and titanium in an amount not exceeding 0.2% each, the balance except for impurities being iron, and the chromium and carbon contents being such that $Cr + 100C = 23.5$ to 30.

3. Stainless steel containing from 0.07 to 0.11% carbon, from 16.5 to 17.5% chromium, from 3.5 to 4.5% nickel and not more than 0.05% nitrogen, together with manganese with or without either silicon or tungsten in amounts such that $Mn + \frac{11}{7}Si + W = 2.5$ to 3.5%, the balance except for impurities being iron.

4. Stainless steel containing from 0.11 to 0.16% carbon, from 14.0 to 16.5% chromium, from 3.5 to 4.5% nickel and not more than 0.05 nitrogen, together with manganese with or without either silicon or tungsten in amounts such that $Mn + \frac{11}{7}Si + W = 2.5$ to 3.5%, the balance except for impurities being iron, and the chromium and carbon contents being such that $Cr + 100C = 23.5$ to 30.

5. Stainless steel according to any of the preceding claims except that it also contains copper not exceeding 4%, and that

$$Mn + \frac{11}{7}Si + \frac{2}{3}Mo + \tfrac{1}{2}Cu = 2.5 \text{ to } 3.5.$$

6. Stainless steel according to claim 5 in which the copper content is from 1.5 to 3.5%.

7. Stainless steel containing from 0.07 to 0.11% carbon, from 16.5 to 17.5% chromium, from 3.5 to 4.5% nickel, not more than 0.05% nitrogen and from 2.5 to 3.5% manganese, the balance except for impurities being iron.

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PROVISIONAL SPECIFICATION

No. 16125 A.D. 1957

Improvements relating to Alloy Steel

We, THE UNITED STEEL COMPANIES LIMITED, a British Company, of 17, Westbourne Road, Sheffield 10, do hereby declare this invention to be described in the following statement:—

It is known that by suitable control of chemical composition it is possible to obtain a stainless steel in which the austenite either does or does not transform to martensite on cooling to room temperature, the steel being austenitic if the transformation range is below room temperature and martensitic if it is above.

The production of a stainless steel in which the transformation will take place within a given narrow range is somewhat difficult because a variation in any alloying element alters the transformation range. Moreover, nearly all alloying elements tend to form delta ferrite, which is undesirable since it leads to a reduction in strength and also makes the steel difficult to hot-work. The only alloying elements which do not tend to produce delta ferrite are carbon, nitrogen, nickel, copper and manganese.

We have discovered that if we make stainless steels of certain specific compositions they will contain less than 15% delta ferrite in their microstructure and their martensite transformation range will be confined to a range of approximately 100°C. below room temperature. The steels according to the invention contain from 0.07 to 0.11% carbon, from 16.5 to 17.5% chromium, from 3.5 to 4.5% nickel and not more than 0.05% nitrogen. They also contain manganese with or without silicon or tungsten or both. It is these three last-mentioned elements which are important in producing the desired properties, and the following equation must be satisfied

$$Mn + \frac{11}{7}Si + W = 2.5 \text{ to } 3.5\%$$

It is most convenient to add either silicon or tungsten together with a small amount of manganese or a larger amount of manganese without any silicon or tungsten. Thus the preferred steels have the following contents of these elements: